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Published in:
Materials Science & Smart Materials (MSSM)

Published: 01/01/2018

Document Version
Publisher's PDF, also known as Version of record

[Link to publication on the UWS Academic Portal](#)

Citation for published version (APA):

Abbas, Q., & Mirzaeian, M. (2018). Effect of nitrogen doping on physical and electrochemical properties of resorcinol / formaldehyde based carbons. In A. G. Olabi (Ed.), *Materials Science & Smart Materials (MSSM): Proceedings of the 5th International Conference on Materials Science and Smart Materials* (pp. 430-436). University of the West of Scotland.

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EFFECT OF NITROGEN DOPING ON PHYSICAL AND ELECTROCHEMICAL PROPERTIES OF RESORCINOL / FORMALDEHYDE BASED CARBONS

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ABSTRACT

Nitrogen doped resorcinol (R) and formaldehyde (F) based polymeric gels were synthesised by polymerisation reaction. Nitrogen heteroatoms were incorporated in the bulk network of polymeric gels using melamine as nitrogen source. The resultant aerogels were carbonized at a temperature range 750 to 900 °C under Ar to prepare nitrogen doped carbon aerogels used as the electroactive material for the fabrication of electrodes for electrochemical capacitor. The porous structure of carbon aerogels was characterised by nitrogen adsorption-desorption. Contact angle measurements were performed to investigate the wettability of the electrodes toward the electrolyte when used in the electrochemical cell. The electrochemical properties of the carbon aerogels were characterized by, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The experimental results revealed that resorcinol / catalyst (R/C) and resorcinol / melamine (R/M) ratios played crucial role in the development of porous structure (specific surface area, average pore size and pore size distribution) of the resultant carbons. Nitrogen content played an important role to improve wetting behaviour and capacitive performance of the electroactive material. The carbon material MRFC-100-800-R/M80 with an R/C ratio of 100 and an R/M ratio of 80 carbonized at 800 °C exhibited much improved wettability with 6 M KOH showing considerable decrease in the contact angle from 125° to 103°. Improved capacitance of 208 Fg⁻¹ was achieved for N-doped carbon sample MRFC-100-800-R/M80 as compare to the specific capacitance of 136 Fg⁻¹ for an un-doped carbon prepared under similar conditions.

Keywords: Nitrogen doping, Surface chemistry, Capacitive performance, Electrochemical characterisation

1 INTRODUCTION

Renewable sources of energy such as solar, wind and tidal have acquired significant importance recently due to environmental concerns and increased cost / demand of energy. However, due to their intermittence nature power management and energy storage has become increasingly important issue. Most desirable electrical energy conversion and storage devices include fuel cells, batteries and electrochemical capacitors. Electrochemical capacitors also known as super capacitors or ultra-capacitors are emerging energy storage devices and considered as one of the most promising energy storage technology owing their distinct properties such as exceptionally high power densities, excellent cycle-ability and efficiency as compare to other electrochemical devices such as fuel cells and batteries[1, 2].

Electrode and electrolyte materials are the key components affecting the performance of electrochemical capacitors. Variety of carbon based materials such as graphene, carbon nanotubes, carbide derived carbons, carbon nano-fibres and carbon aerogels and aqueous, organic and ionic solutions have been adopted as electrode and electrolytes respectively [3-6]. Since carbon aerogels possess properties such as cost effectiveness, ease of processability, chemical inertness and controllable porosity makes them the most appropriate electrode material to be adopted in electrochemical capacitors.

High capacitive performance has been reported when controlled porosity carbon aerogels were used as electrode material where pore diameter was comparable to the ion size of adapted electrolyte [7, 8]. Specific capacitance can be further enhanced by introducing nitrogen and oxygen the functional groups on the surface or into the matrix of the electroactive material [2, 9] . Recently nitrogen doped carbon aerogels have been extensively explored due to its large specific surface area, good chemical stability and enhanced wettability. However most often functional groups are introduced on the surface of the carbon material using reagents such as KOH or amino acid to introduce pseudo-capacitance and to improve wettability to the electrolyte which results in reduced electrode / electrolyte resistance [10, 11].

Here, we report the synthesis of highly porous nitrogen doped polymeric carbon aerogels with exceptionally high specific surface area, controlled pore size distribution and suitable nitrogen content synthesised by sol-gel polycondensation reaction between Resorcinol (R) and Formaldehyde (F). Nitrogen is introduced into the bulk using melamine as a nitrogen source where nitrogen content is controlled by controlling the resorcinol / melamine (R/M) molar ratio. Electrochemical characterisation shows that nitrogen containing electroactive material show improved capacitive performance when used with 6M KOH as an electrolyte. The effects of the R/M ratio on the pore development, specific surface area, and the capacitive performance and the wettability of the obtained nitrogen-doped porous carbons are analysed using cyclic voltammetry and electrochemical impedance spectroscopy and contact angle measurements.

2 EXPERIMENTAL

2.1 Synthesis of RF and mR/F Aerogels

Resorcinol/ formaldehyde aerogels were prepared according the procedure described elsewhere [7]. Nitrogen doped resorcinol (R) formaldehyde (F) aerogels gels were synthesized using the same procedure however, melamine was used as a nitrogen source. For the preparation of melamine-resorcinol-formaldehyde (mRF) gels, RM solution was prepared by mixing the predetermine amount of resorcinol and melamine (M) in distilled water (W) at room temperature and the catalyst (C) was added. The solution was heated to 80 °C and mixed under vigorous stirring for 45 mins. The solution was cooled down and F was added and kept on stirring for another 45 mins at room temperature. R/F and R/W (gml⁻¹) were kept constant at 0.5 (which is considered as the stoichiometric ratio) and 0.1 respectively whereas R/M ratio was varied between 20 and 120. The homogenous solution was placed in oven at 25 °C for 24hrs to allow the gelation process to start in sealed glass vials to prevent the evaporation of water during the gelation process. Temperature was increased to 60 °C for 72hrs and finally temperature was increase to 80 °C and maintained for 48hrs. Gels were submerged in acetone for solvent exchange to replace water with acetone from gel structure prior to vacuum drying. Finally, the gels were dried in a vacuum oven at 64°C for 4 days.

2.2 Carbonization of mR/F and RF aerogels

Calcination of the dried RF and mRF aerogels was performed at 800 °C temperatures for 3hrs to investigate the effect of pyrolysis conditions on the porous structure of carbon aerogels and the carbonization processes has been described elsewhere [7].

2.3 Electrode fabrication

Electrodes for electrochemical measurements were prepared using carbon in the form of well grinded powder. Approximately 80 wt% active carbon material, 10 wt% Cabot carbon black XC72 as conductivity enhancer and 10 wt% Kynar 2801as binder were used for the fabrication of electrodes. The electrode components were mixed with acetone for 2 hrs to form a paste. The paste then was rolled into sheets with wet film thickness of 250 µm using applicator. Circular discs with diameter of 1.33 cm were then punched out from the films and dried overnight in a vacuum oven at 85 °C resulting in a dry thickness for the electrodes in the range of 10 – 20 µm.

3 PHYSICAL CHARACTERIZATION

The porous structure of MRF/RF carbon aerogels was characterized by a Tri-Star adsorption analyser (Micromeritics). The samples were evacuated in a vacuum oven at 80 °C at 5 mbar for 24 h and then they were further purged in a nitrogen flow at elevated temperatures (80 °C for gels samples and 300 °C for carbons) in a Flowprep system (Micromeritics) prior to the adsorption/desorption measurements. BET method was used for surface area measurements, t-plot method was used for micropore analysis, and BJH method using adsorption branch of the isotherm was used to calculate pore size distribution. The total pore volume was determined from the adsorbed volume of nitrogen at saturation pressure (P/Po = 0.99) [12].

Contact angle measurements were carried out using a CAM 200 goniometer system manufactured by KSV Ltd based on video captured images and automatic image analysis using CAM software. 6M KOH was used as the probing liquid for the determination of contact angles.

3.1 BET analysis of the samples

The porous structure of un-doped and nitrogen doped carbon aerogels was characterized by a Tri-Star adsorption analyser (Micromeritics). The samples were evacuated in a vacuum oven at 80 °C at 5 mbar for 24 hrs followed by further purging in nitrogen flow at 300 °C in a Flowprep system (Micromeritics) prior to the adsorption/desorption measurements. BET technique was used for surface area measurements, t-plot method was adopted for micropore analysis, and BJH method using adsorption branch of the isotherm was used to calculate pore size distribution. The total pore volume was determined from the adsorbed volume of nitrogen at saturation pressure ($P/P_0 = 0.99$) [12].

Figure 1 shows adsorption-desorption isotherms of un-doped (RFC) and (mRFC) nitrogen doped (different R/M ratios) carbon aerogels. A significant increase in adsorption at lower $P/P_0 < 0.2$ shows the development of microporosity whereas hysteresis loops at higher relative pressure P/P_0 between 0.2 – 1.0 indicates the existence of meso-porosity in the samples [13].

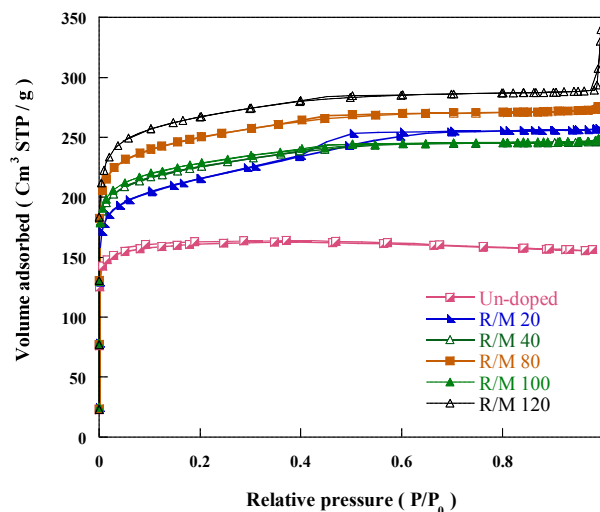


Figure 1 adsorption-desorption isotherms of un-doped (RFC) and (mRFC) nitrogen doped (different R/M ratios) carbon aerogels.

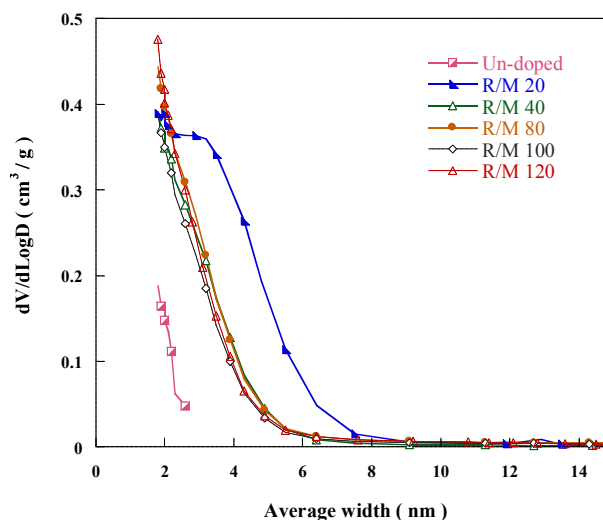


Figure 2 Pore size distribution of un-doped and nitrogen doped (different R/M ratios) carbon aerogels.

Pore size distribution (PSD) of all the samples represented in figure 2 show that all the sample are predominantly microporous in nature and pore size distribution is centred around 2 nm.

Table1 Porosity parameters of un-doped and nitrogen doped (different R/M ratios) carbon aerogels.

Sample	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	V _{micro} (cm ³ g ⁻¹)	V _{meso} (cm ³ g ⁻¹)	V _{micro} %	V _{meso} %	D _{ave} (nm)
RFC100-undoped	537	0.2420	0.2167	0.0253	90	10	1.80
mRFC 100-RM20	723	0.4001	0.2209	0.1792	55	45	2.21
mRFC 100- RM40	744	0.3848	0.2554	0.1294	66	34	2.07
mRFC 100- RM80	841	0.4304	0.2833	0.1471	66	34	2.05
mRFC 100- RM100	762	0.3880	0.2634	0.1246	68	32	2.04
mRFC 100- RM120	900	0.5259	0.3072	0.2187	58	42	2.34
mRFC 100- RM140	899	0.4931	0.3096	0.1835	63	37	2.19

3.2 Contact angle measurements

The wettability of carbon aerogel (RFC) /Nitrogen doped carbon aerogel (mRFC) was investigated when 6M KOH was used as the probing liquid for contact angle measurements. Appropriate surface modification, surface roughness, surface energy and the type of electrolyte adopted can have a significant effect on the wettability of the surface. It has been observed that nitrogen or oxygen modified surfaces interact with aqueous electrolyte with increased wettability due to the presence of nitrogen or oxygen functional groups [14].

Table 2 contact angle measurements of un-doped and nitrogen doped carbon aerogels

Sample	RFC100-800	mRFC100-800
Contact angle	125°	103°

Table 2 shows the results of wettability of the carbon electrode improved and decrease in contact angles from of 125° to 103° was observed. This improved wettability is mainly contributed by nitrogen functional groups on the carbon surface.

4 ELECTROCHEMICAL CHARACTERIZATION

Specific capacitance for the electrode was calculated from the following equation:

$$C = \frac{I}{\left(\frac{dV}{dt}\right)} \quad (1)$$

Where ‘*I*’ is the average discharge current and dV/dt is the scan rate. The specific capacitance *C_{sp}* in Fg⁻¹ was calculated by:

$$C_{sp} = 2 \times C / m \quad (2)$$

Where ‘*C*’ is the measured capacitance for two-electrode cell and *m* is the mass of active material in one electrode.

4.1 Electrochemical Analysis

The specific capacitance of the carbon samples is calculated using the equations 1 and 2. It has been observed that with the increase in R/M ratio (decrease in nitrogen content), specific capacitance (SC) improved whereas decline in specific capacitance was observed when ratio increased beyond R/M 80 as shown in table 3. The CV loops are gradually depressed and specific capacitance decreases as the scan rate increases. This can be mainly attributed to the kinetic effects and poor ion diffusion at higher scan rates [15]. Table 3 shows that significantly improved specific capacitance of 208 Fg⁻¹ for doped carbon as compared to

136 Fg^{-1} for un-doped carbon. Our results show that since there was no significant change in porous parameters so the improvement in the capacitance is mainly contributed by nitrogen functional groups.

Table 3 capacitive performance of supercapacitor at different scan rate in 6M KOH electrolyte

R/M ratio	Specific surface area (m^2g^{-1})	Specific Capacitance (Fg^{-1})		
		Scan rate (mVs^{-1})		
		5	10	15
Un-doped	537	136	71	51
20	723	29	13	8
40	744	79	19	11
80	841	208	70	19
100	761	198	63	32
120	900	141	42	29

Porous parameters of un-doped /doped carbons are shown in table 1 since change in the pore size is negligible (approx. 2nm) the increase in SC is mainly due to the introduction of nitrogen. SSA for the carbon R/M 120 is higher than the carbon with R/M 80 which indicates that R/M80 gives the optimum value of nitrogen and results in highest SC.

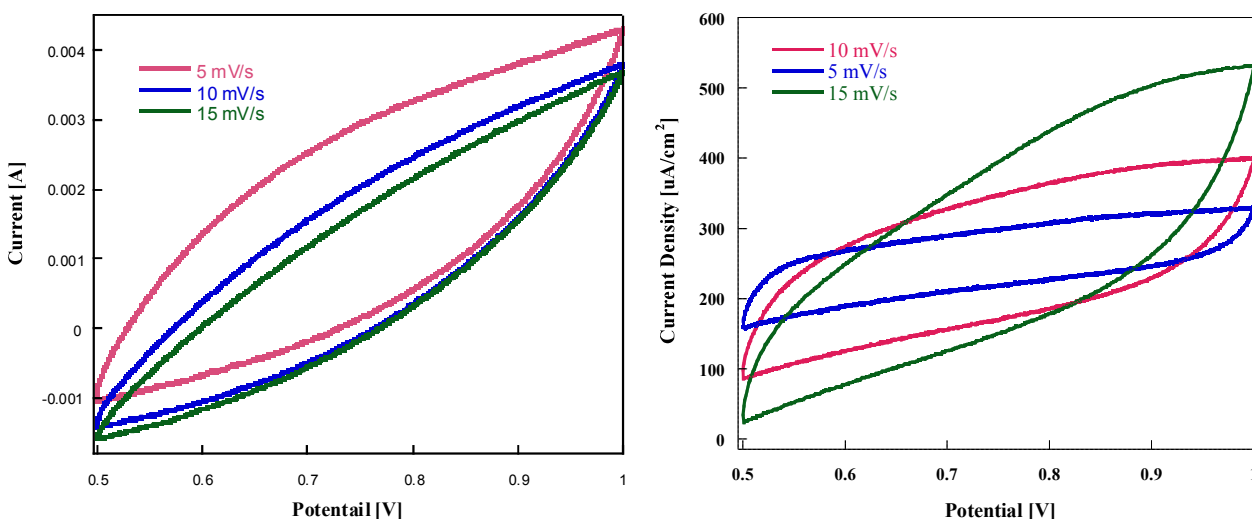


Figure 3 Cyclic Voltammogram (CV) of the cell using un-doped and nitrogen doped carbon aerogels as electroactive material at different scan rates.

Electrochemical impedance spectroscopy (EIS) is very useful technique to analyse the resistive and capacitive behaviour of the materials [16]. Figure 6 shows Nyquist plot for cell using carbons with different R/C ratios as electroactive material in the frequency range of 100 KHz to 50 Hz.

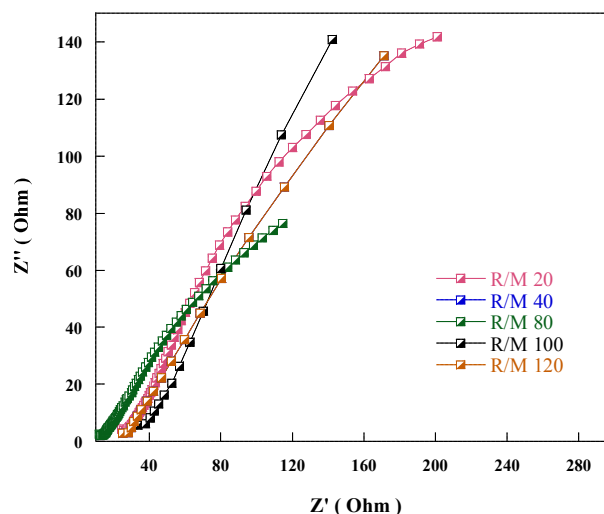


Figure 6 EIS spectra of carbon aerogels with different R/M ratios

5 CONCLUSIONS

Resorcinol/formaldehyde carbon aerogels (RFC) and nitrogen doped carbon aerogel (mRFC) were synthesised by sol-gel polymerisation where nitrogen doping into the matrix of the bulk carbon was achieved using melamine as nitrogen source, nitrogen content was controlled through variation in resorcinol/melamine (R/M) ratio.

The effect of nitrogen doping on porosity, surface characteristics and electrochemical properties of these doped and un-doped polymeric carbon aerogels was evaluated when used as electrode in a supercapacitor cell. Improved specific capacitance and enhanced wettability was observed after the introduction of nitrogen functional groups within the matrix of carbon aerogels however, porous parameters including pore size and specific surface area have seen negligible change after nitrogen doping. Higher specific capacitance of 208 Fg⁻¹ for nitrogen doped carbon (mRFC100-800 R/M80) as compared to 136Fg⁻¹ for and un-doped carbon (RFC100-800) at the scan rate of 5mVs⁻¹ was achieved where both doped and un-doped carbons were prepared under similar conditions and possess comparable porous characteristics. Improved wetting behaviour and specific capacitance is believed to be contributed by nitrogen functional groups when adopted as electroactive material.

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